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14. ABSTRACT
Fielded pyrotechnic compositions containing the environmentally-hazardous oxidizer potassium perchlorate are highly scrutinized due to increasing government regulations to limit ground water contamination. A perchlorate-free yellow flare composition for future implementation into the Mk 144 Yellow Signal Flare is presented. The reformulated yellow signal flare composition was developed by employing a "color mixing" technique which utilizes sodium nitrate, barium nitrate, and polyvinyl chloride as alternative oxidizers to produce Na emission lines in the orange region of the spectrum and BaCl and BaOH emission lines in the green region of the spectrum. By utilizing this approach, the resulting dominant wavelength of this perchlorate-free flare appears yellow to an observer. The combustion characteristics of the perchlorate-free yellow flare compositions are documented using 15- gram pellet linear burn rate experiments instrumented with high-speed imaging, a tri-stimulus detector to document the illuminance and a visual spectrometer to document the spectral intensity. The in-service yellow perchlorate-containing formulation was tested side-by-side with the perchlorate-free versions for comparison purposes. Specifically, the burn rates were reasonably similar, the luminous intensity of the perchlorate-free versions was slightly higher, and dominant wavelengths and color purities were also comparable to slightly improved. Since the perchlorate-free replacement composition is intended to be of lower environmental impact, the combustion residue from the in-service and perchlorate-free compositions were analyzed via mass spectrometry techniques to attempt to identify environmentally hazardous species (e.g., perchlorates). Experimentally identified combustion products will be compared to that predicted from the thermochecmical equilibrium code NASA CEA.

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perchlorate-free, yellow light, environmentally friendly, flare, pyrotechnic

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Elimination of Perchlorate Oxidizers from Yellow Pyrotechnic Flare Compositions

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Elimination of Perchlorate Oxidizers from Yellow Pyrotechnic Flare Compositions

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Prepared for: EuroPyro

May 5, 2015, Toulouse, France

Dr. Adam Razavian, SES
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Problem

Many in-service pyrotechnics utilize high performance toxic fuels/oxidizers:

- **Perchlorates ($KClO_4$, NH_4ClO_4)**
- Chromates ($BaCrO_4$, $PbCrO_4$)

Army and Navy laboratories are working to remove toxic ingredients from pyrotechnics

Tasked with removing energetic oxidizers while maintaining or increasing performance

Available Options

- Reformulate with available environmentally friendly chemicals (can be difficult)
- Develop/wait for new energetics

High performance pyrotechnics has historically been achieved with toxic ingredients

In-Service Mk 144 Composition
Mg / $Ba(NO_3)_2$ / $KClO_4$ / NaC_2O_4 / Asphaltum / Epoxy

Project Description

Project Description: The goal is to develop a perchlorate-free yellow flare composition for use in the Mk 144 signal flare (regards to the Mk 144 performance specifications) and will obtain safety sensitivity data to support transition of the composition from laboratory to concept scale.

>130 g of perchlorate-containing pyrotechnic
Approximate >30 g of $KClO_4$ per candle

Image of signal flare (left) and full Mk 144 flare at NSWC ordnance testing area (right)

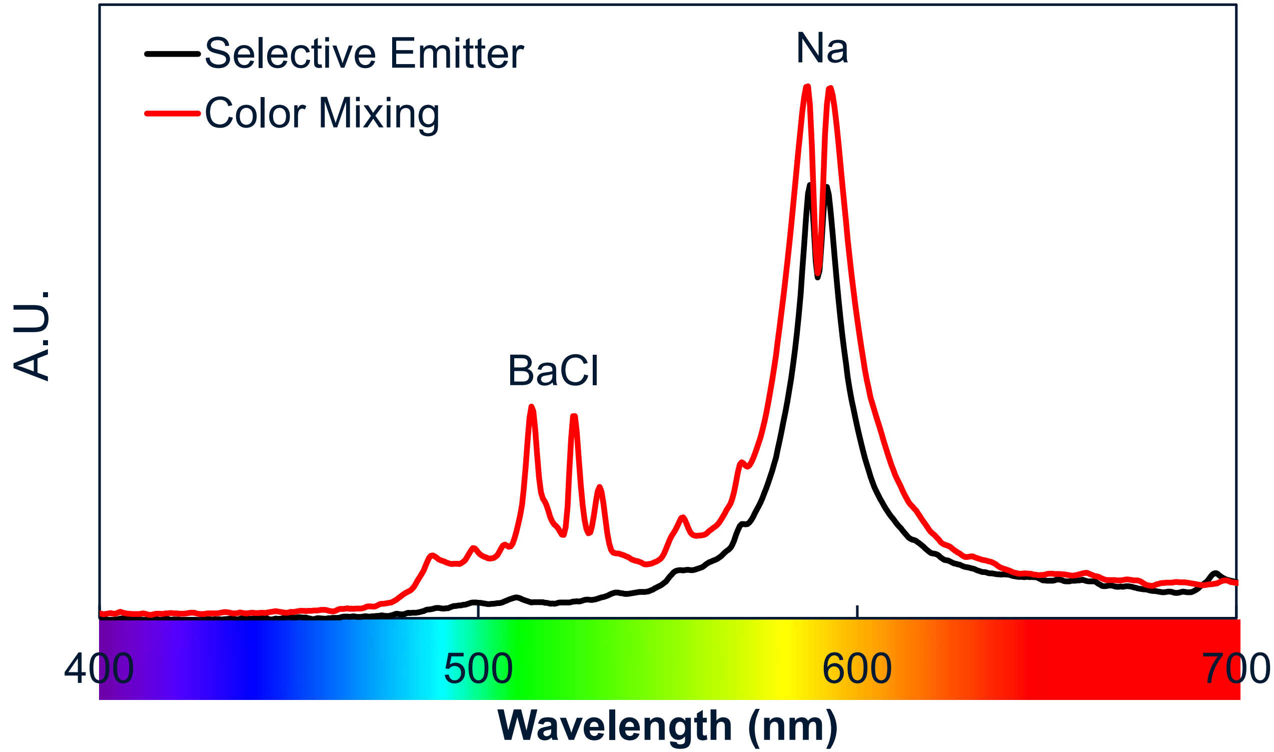
Overview of Experimental Work

- Theoretical calculations
- Overview of promising formulations
- Effect of particle size on combustion performance
- Effect of NaC_2O_4 on $Mg/NaNO_3$/binder combustion performance
- Ignition Sensitivity of Selected Compositions
  - Effect of binder content on ignition sensitivity
- Summary

Function test of Perchlorate-free green Mk 141 at Crane's Ordinance Testing Area

How to make colored flame?

1. Selectively Emit - Produce a hot combustion product species that emits at the exact wavelength that you want (rarely possible)
2. Mix colors so the average wavelength is that of the desired color (must be careful of color purity requirements)



Unfortunately, human eyes are not perfect detectors…

Theoretical Predictions

$Mg + Mg_{0.5}Al_{0.5} + NaNO_3 + Ba(NO_3)_2 + Na_2C_2O_4 + KClO_4 + PVC +$ Hydrocarbon binders → $MgO + Na + BaCl + BaOH + HCl +$ others

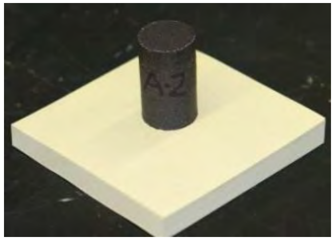
With known combustion velocity and luminosity requirements, predicting combustion temperature is a good place to start…

	Mk144-Std	YSF-1	YSF-3	YSF-8	YSF-12
Mg	**	28.10	23.00	20.10	26.0
$Mg_{0.5}Al_{0.5}$	--	--	3.60	--	--
$NaNO_3$	--	20.00	27.40	37.00	39
$Na_2C_2O_4$	**	--	--	--	30
$Ba(NO_3)_2$	**	34.10	29.00	27.05	--
$KClO_4$	**	--	--	--	--
PVC	--	8.90	8.10	10.90	--
Asphaltum	**	3.95	3.95	--	--
Epoxy	**	4.95	4.95	4.95	5
T_{ad} (K)	1986	2349	2156	2813	2688

Three best compositions!

Experimental Setup

- Due to the scale of laboratory experiments (15g pellets vs 140g candle), compare all results to 15g pellet of in-service formulation



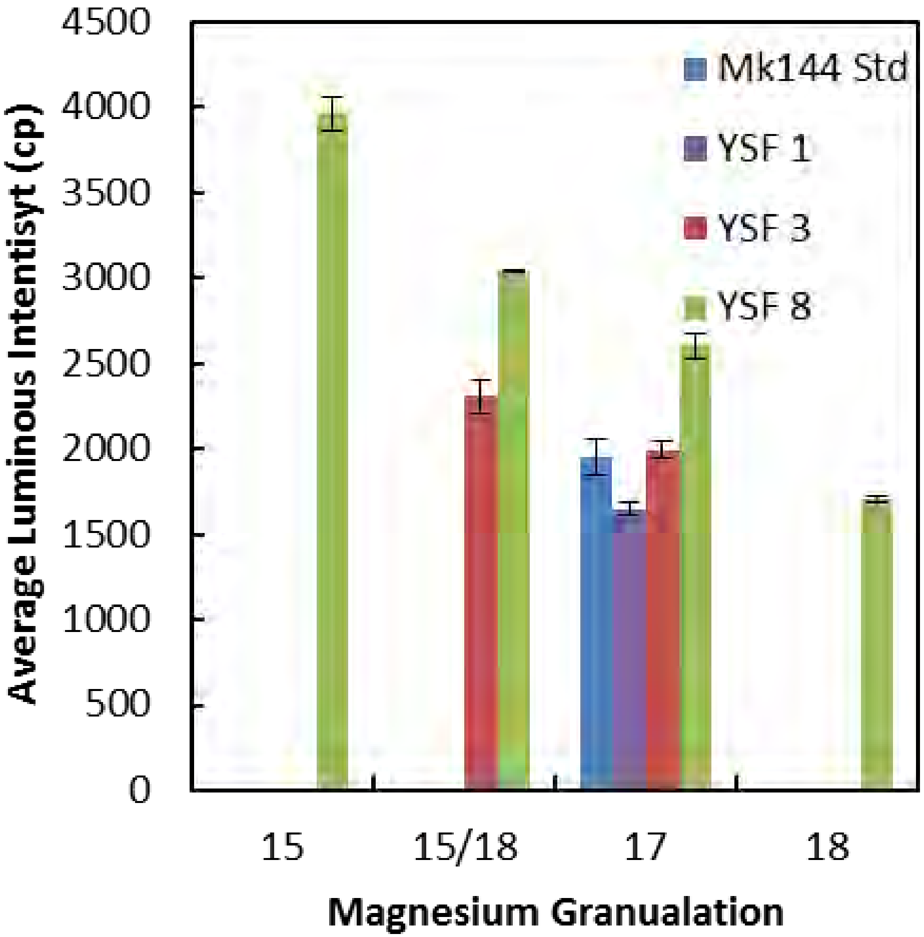
15g reactive pellet

Perchlorate-free composition

In Service Mk 144 composition

Instrumentation:
- Photopic intensity measurement: SED033/Y/W photopic detector (silicon photodiode)
- Color measurement: Optroniks FMS 10 tri-stimulus colorimeter

Effect of Mg size on Luminous Intensity



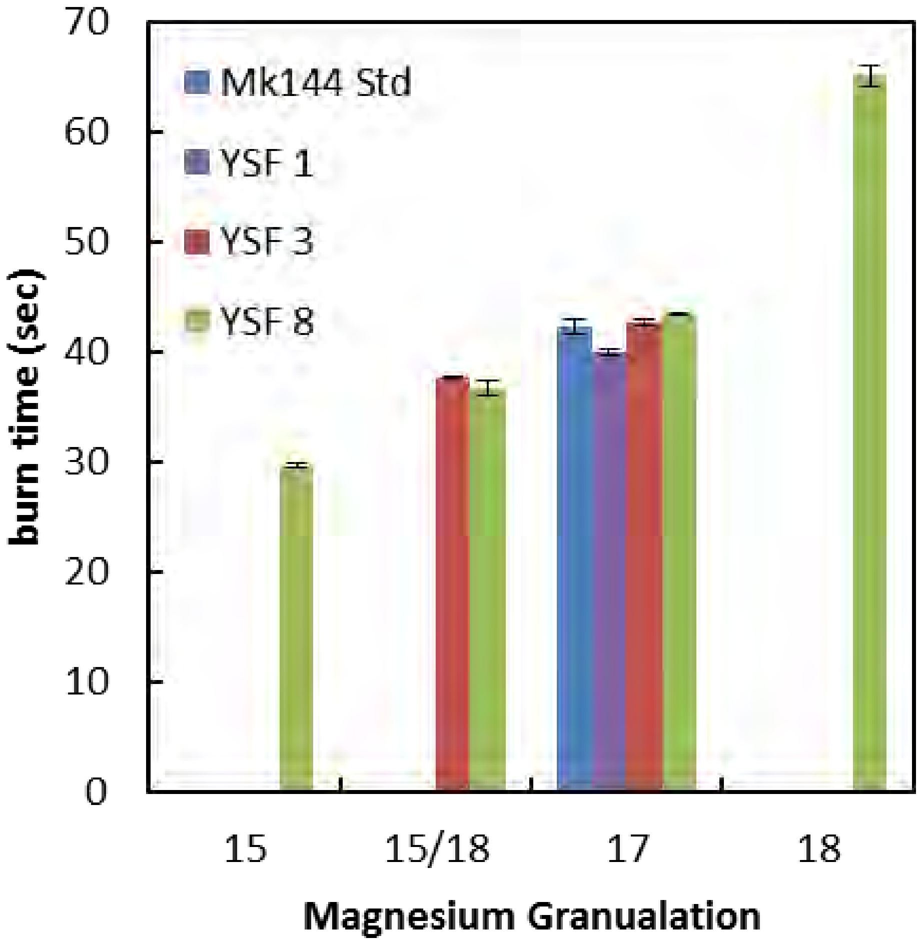
- Average intensity increases with finer magnesium
- YSF 3 and 8 all have similar burn times to that of the standard
- YSF 1 is slightly slower than the standard
- *All compositions meet dominant wavelength and color purity requirements*

Notes:

- All Compositions use 5% binder
- Gr 15/18 = 60% Gr 15 + 40% Gr 18

Gr 15 ~ 75 - 125 microns
Gr 17 ~ 150 – 275 microns
Gr 18 ~ 300 – 575 microns

Effect of Mg size on Burn Time



- Burning rate increases with finer magnesium
- YSF 3 and 8 all have similar burn times to that of the standard
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Gr 15 ~ 75 - 125 microns
Gr 17 ~ 150 – 275 microns
Gr 18 ~ 300 – 575 microns

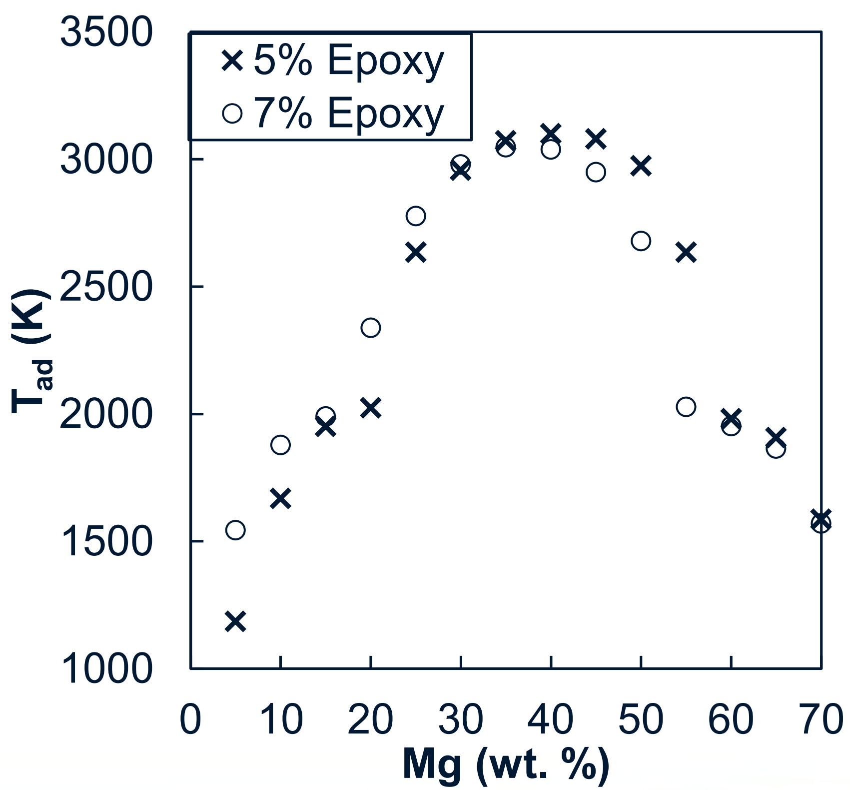
Effect of NaC_2O_4 on $Mg/NaNO_3$/binder

Thus far:

In-service composition: Mg / $Ba(NO_3)_2$ / $KClO_4$ / NaC_2O_4 / Asphaltum / Binder

YSF 3: Mg / $Mg_{0.5}Al_{0.5}$ / $NaNO_3$/ $Ba(NO_3)_2$ / PVC / Asphaltum / Epoxy

Can we make a simpler yellow-flare composition… start with Mg / $NaNO_3$ / Epoxy

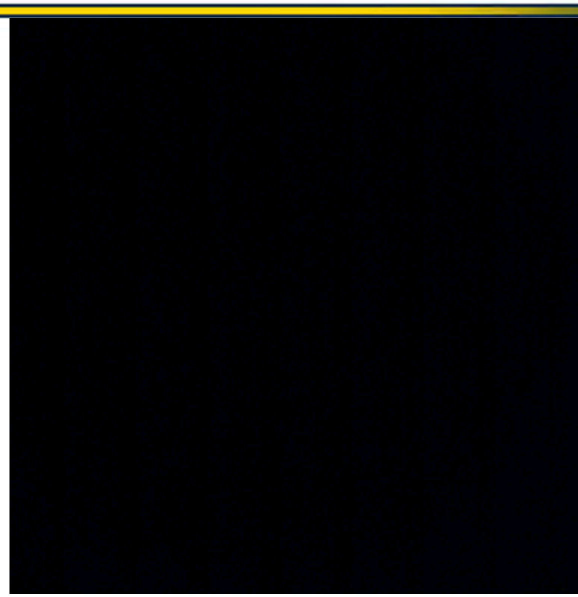


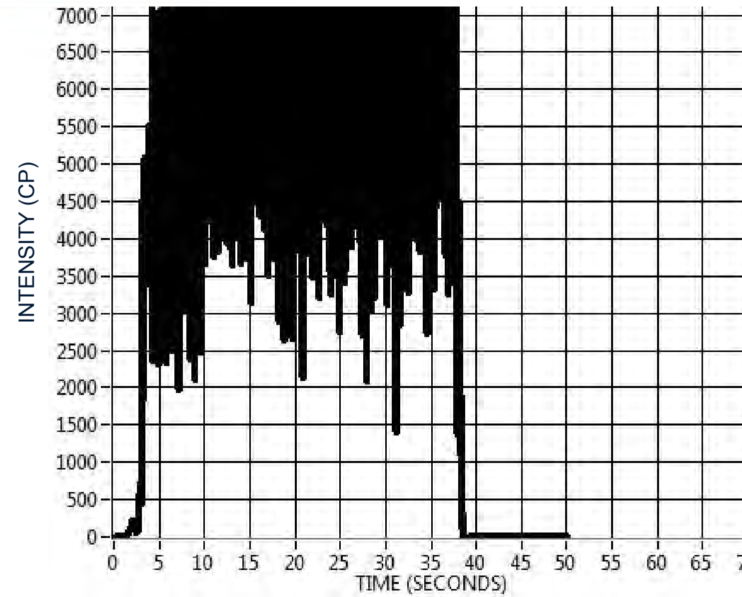
Previous results show that ~2500 K will result in desirable burn times

- $Mg/NaNO_3$/Epoxy (26/69/5 wt. %)

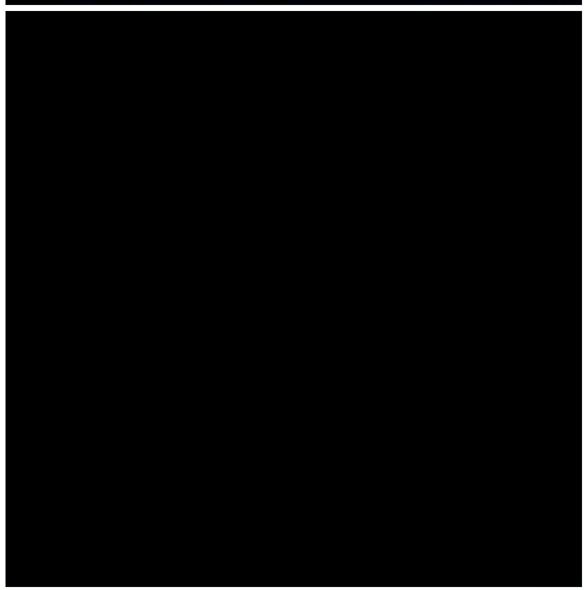
Effect of NaC_2O_4 on $Mg/NaNO_3$/binder

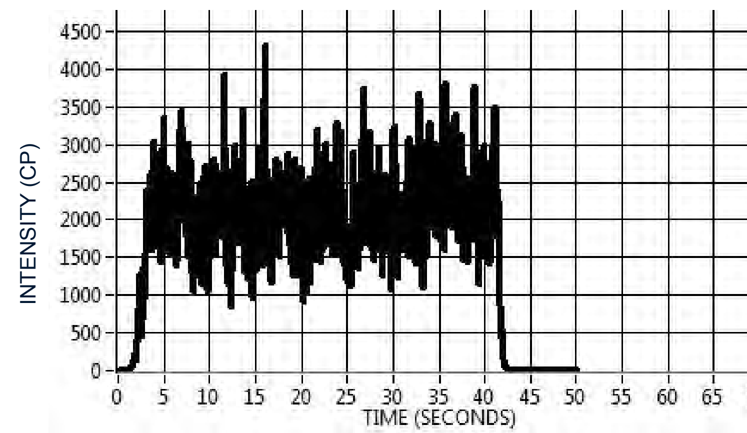
Mg / $NaNO_3$ / Epoxy
(26 / 69 / 5 wt. %)



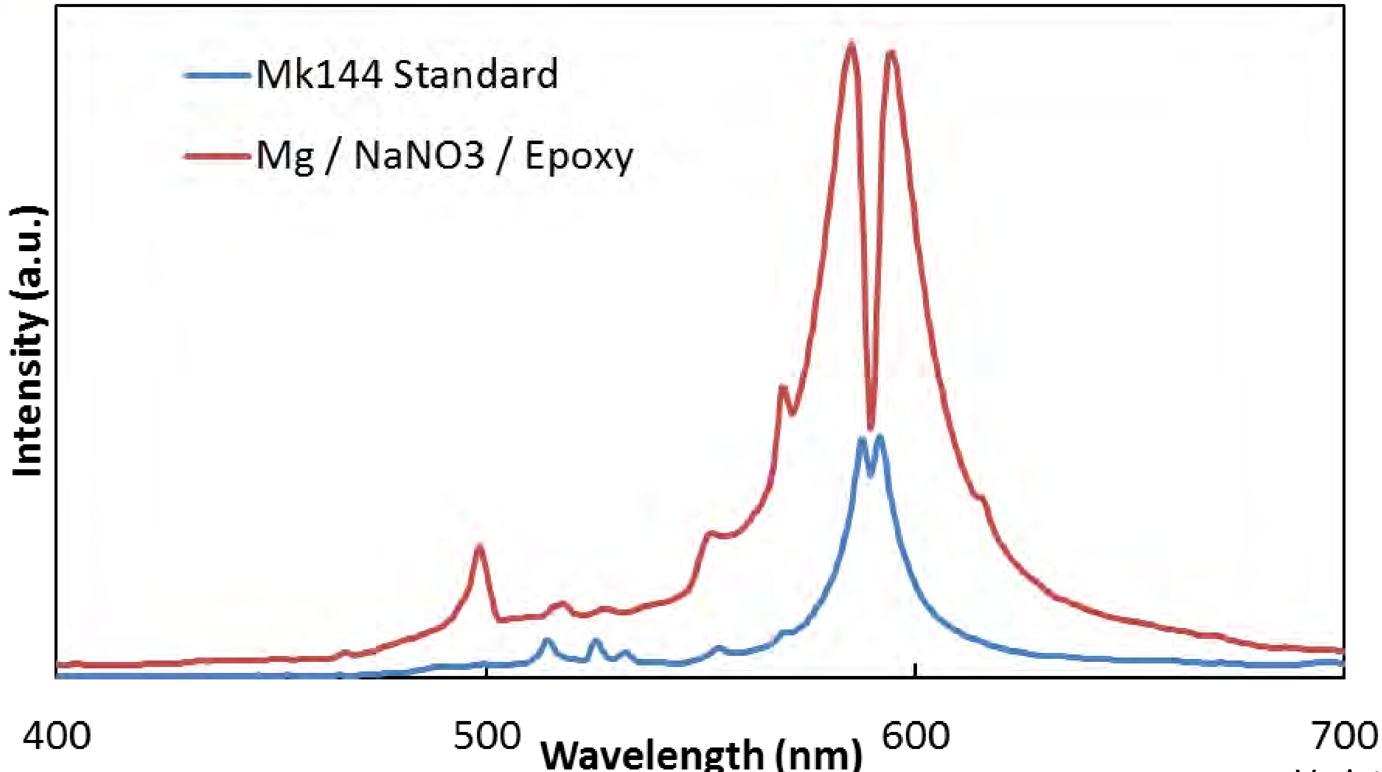


In-service perchlorate
containing formulation
Mg / $Ba(NO_3)_2$ / $KClO_4$ /
NaC_2O_4 / Asphaltum / Epoxy





Effect of NaC_2O_4 on $Mg/NaNO_3$/binder

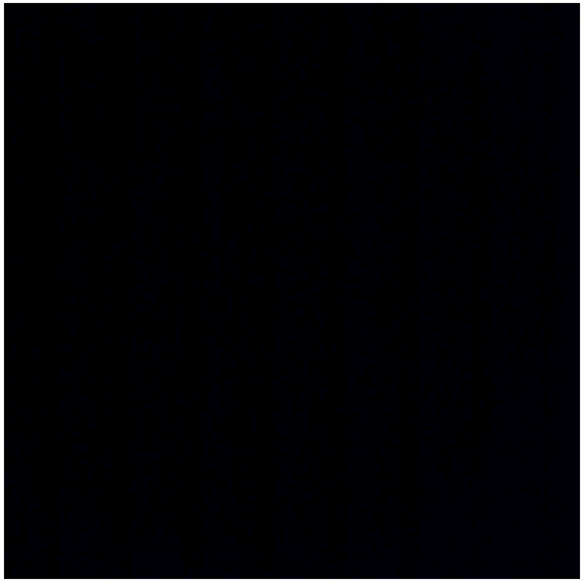


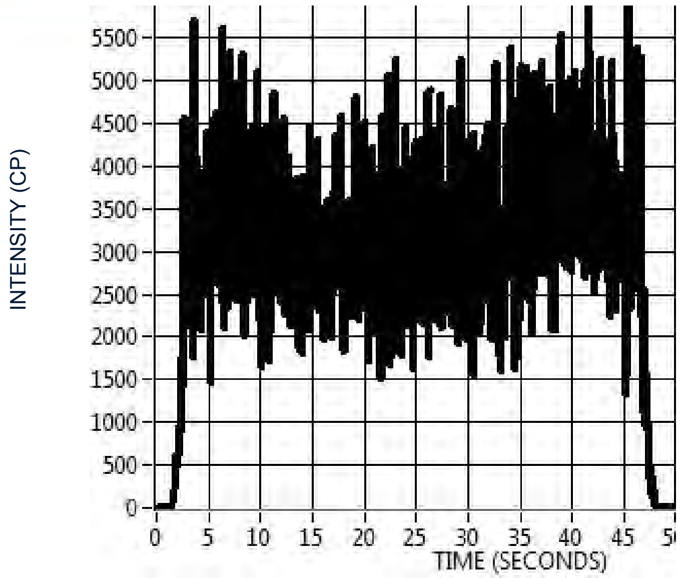
	t (s)	I_v (cp)	λ (nm)	Purity (%)	Variation from Mk 144 Std		
					% t (s)	% Cp	% Purity
Standard Mk144	42.3 ± 0.7	1949.4 ± 101.3	586.8 ± 0.4	89.1 ± 0.4	--	--	--
Mg / $NaNO_3$ / Epoxy	37.5 ± 0.8	5050.0 ± 318.3	588.0 ± 1.7	78.1 ± 0.4	-6.4	135.6	-11.6

To slow down the burn time, cool the reaction and increase the purity, add NaC_2O_4

Effect of NaC_2O_4 on $Mg/NaNO_3$/binder

Mg / $NaNO_3$ / NaC_2O_4
Epoxy
(25.5 / 38.2 / 29.4 / 7
wt. %)





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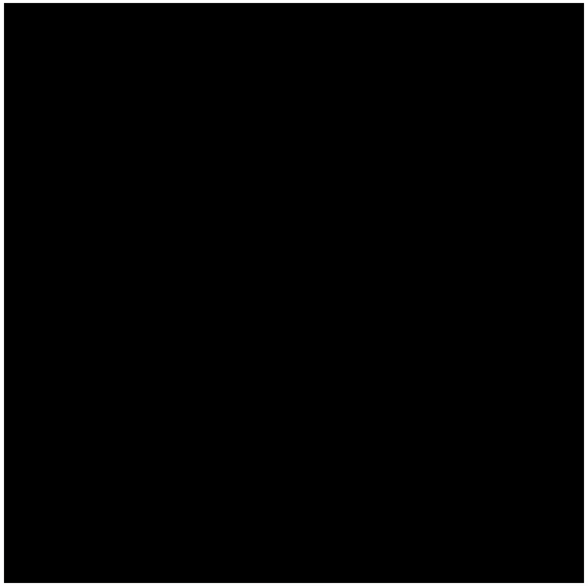
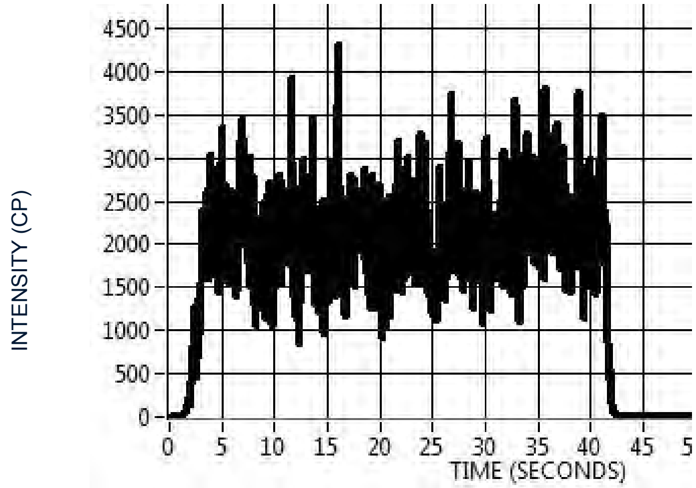
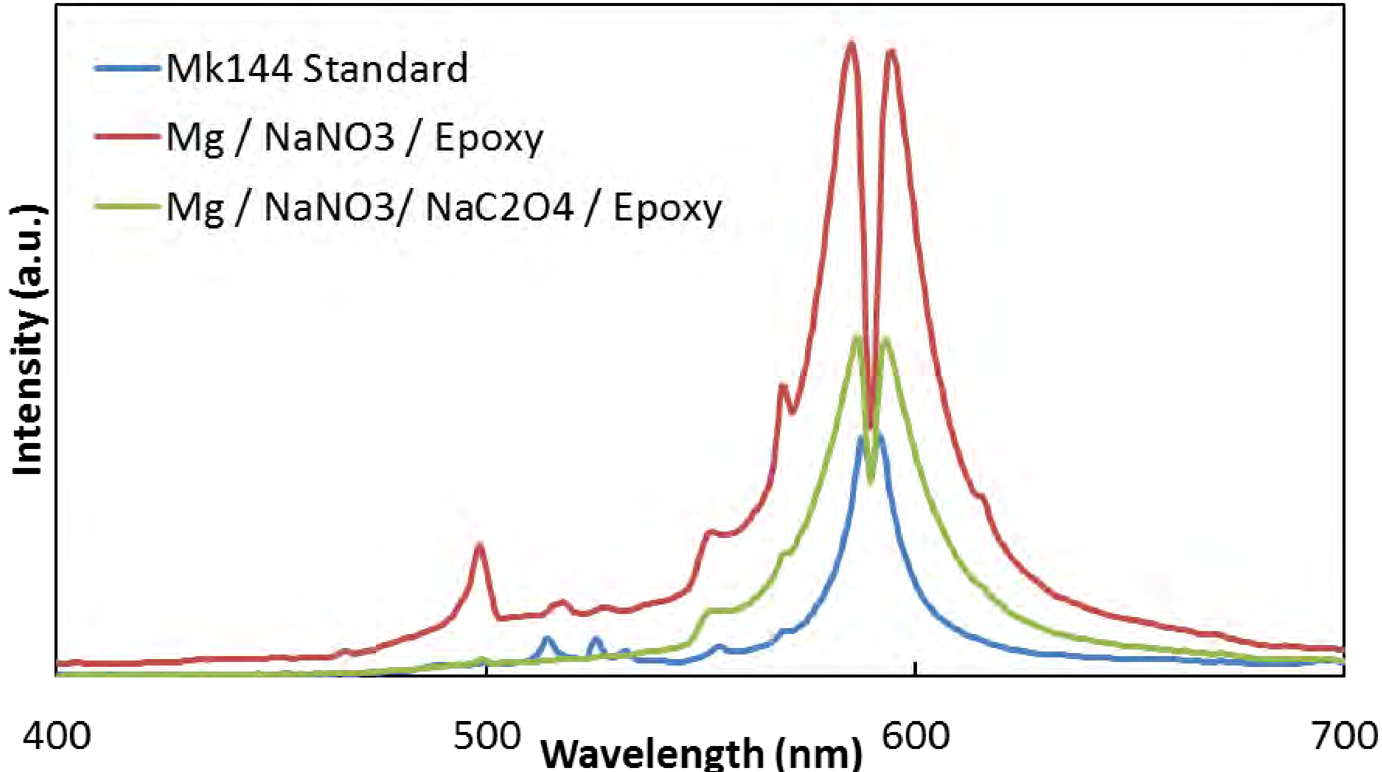




Effect of NaC_2O_4 on $Mg/NaNO_3$/binder



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Mg / $NaNO_3$ / Epoxy	37.5 ± 0.8	5050.0 ± 318.3	588.0 ± 1.7	78.1 ± 0.4	-6.4	135.6	-11.6
Mg / NaNO3 / NaC2O4 / Epoxy	46.2 ± 0.6	3101.5 ± 122.1	587.0 ± 1.0	92.2 ± 0.4	15.5	44.7	4.4

Sensitivity Analysis

All candidate formulations that have similar or higher performance to the Mk144 standard composition, have adequate safety for scale up to concept scale formulation development and testing

- All formulation are insensitive to impact
- Moderate sensitivity to ESD (common)
- Low sensitivity to friction (tends to get better with higher binder content)

	Sample	Impact Sensitivity 50% fire		Friction Sensitivity Energy (ft-lb)		Friction Sensitivity	Electrostatic Sensitivity
		Height (cm)	Energy (J)	Average	Lowest	Response	Maximum No Fire Energy (Joules)
Ref.	RDX Class 5 Type II	89.412	17.520	828.850	116.330	10% Fired	0.080
Mix 5	Mk144 Standard	166.1	32.56	851.92	392.11	60% Fired	0.180
Mix 6	YSF-3 w/7% Binder	178.401	34.97	1001.93	397.81	40% Fired	0.080
Mix 7	YSF-8 w/ 5% Binder	178.401	34.97	881.5	353.97	40% Fired	0.125
Mix 8	YSF-8 w/ 7% Binder	178.401	34.97	1066.82	163.06	20% Fired	0.125
Mix 9	YSF-12 w/ 5% Binder	178.401	34.97	1317.81	288.82	20% Fired	0.125
Mix 10	YSF-12 w/ 7% Binder	178.401	34.97	1266.18	361.71	30% Fired	0.125

Summary

- Identified and refined new perchlorate-free yellow-flare formulations
  - Theoretical calculations
  - Documented effect of particle size on combustion performance to meet both burn time and luminous intensity requirements for various formulations
  - Refined simpler $Mg/NaNO_3/NaC_2O_4$ formulation that still meets requirements
- Ignition Sensitivity of Selected Compositions
  - Effect of binder content on ignition sensitivity

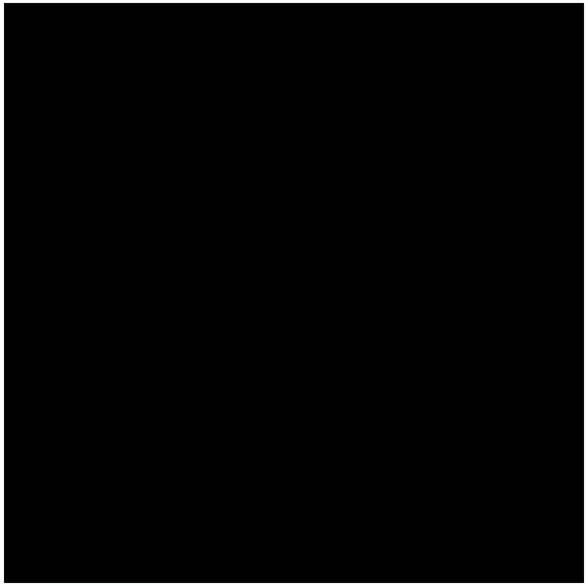
Evaluated dozens of formulations with theoretical calculations and 15 g pellet experiments. Down selected to three perchlorate-free formulations that have similar/improved performance to the in-service formulation for larger scale evaluation

Future Work

- Scale up manufacturing process while verifying safety characteristics
- Evaluate in 140 g candle form factor
- Environmental evaluation perchlorate-free yellow with Pyro-GC-MS
  - Dr Jonathan Dilger IPS presentation

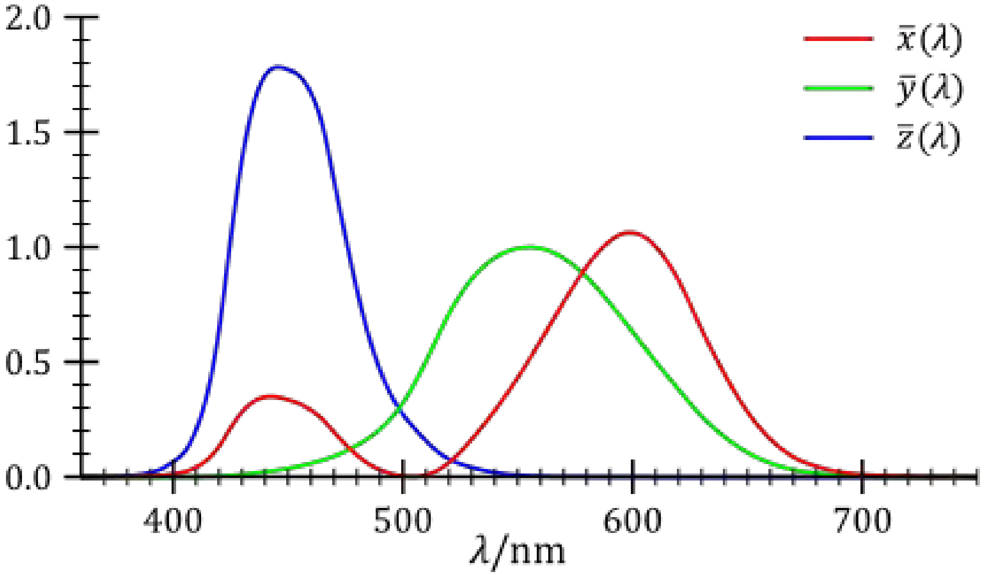
Thanks to collaborators Christina Yamamoto (part owner of patents on YSF 3 & YSF 8) and Dr. Jonathan Dilger

Experimental perchlorate-free formulation



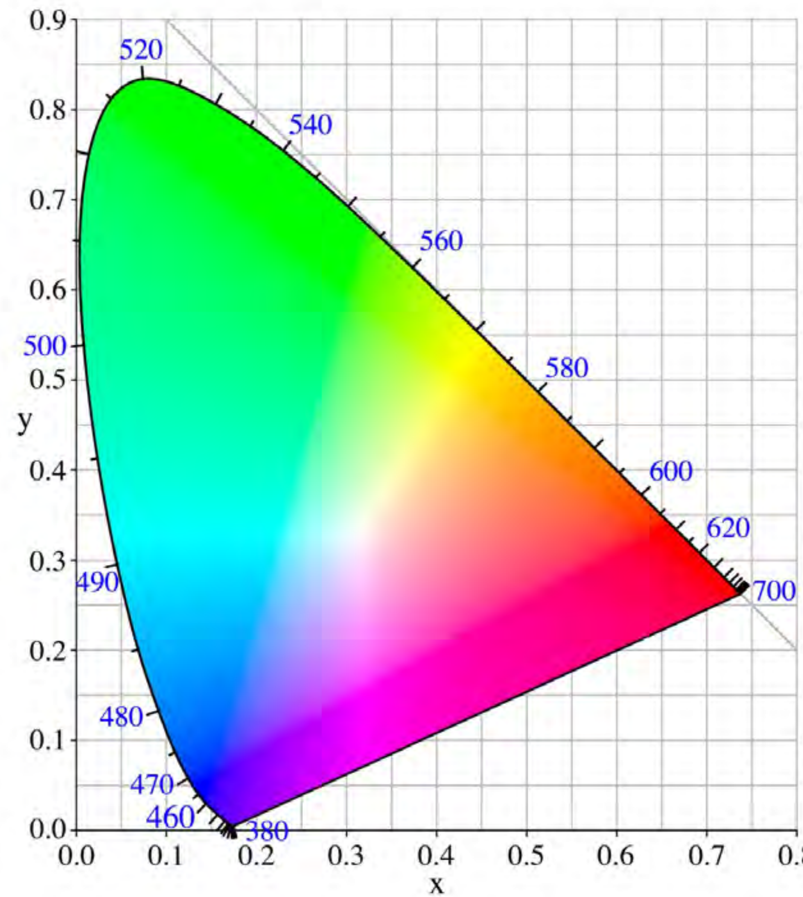
In-service perchlorate containing formulation

Appendix – How we see color



CIE Standard Color Matching Functions

CIE - Commission internationale de l'éclairage



The CIE 1931 color space chromaticity diagram

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